

1.184.321

PATENT SPECIFICATION

DRAWINGS ATTACHED

1.184.321



Inventor: WILLIAM RAY WOLFE

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COMPLETE SPECIFICATION

Electrochemical Cells

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to electromechanical cells having a membrane formed from an ion-exchange resin. More specifically, the invention concerns polymeric fluorocarbon proton ion-exchange membranes employed in electromechanical cells, particularly fuel cells using an acidic electrolyte and secondary cells using electromechanically regenerable electrolytes.

In a fuel cell, a fuel, such as hydrogen or a material which decomposes to hydrogen, is oxidized in an oxidation zone or chamber giving up electrons to an anode. The hydrogen ions formed migrate by means of an ion-exchange resin to the reduction zone or chamber where they combine with oxygen ions from an oxidant reduced at the cathode. Thus, both material and electrical charge balances are maintained as electrons flow from the anode to the cathode. This electron flow can be utilized to provide useful electrical energy.

Heretofore, alkaline electrolytes have been used most frequently in fuel cells. However, the use of acidic electrolytes is desirable, for when carbon-containing fuels are employed, the carbon dioxide formed will not be chemically retained as it is when alkaline electrolytes are used. The use of acid electrolytes has been hindered because of the corrosive nature of the acid environment and because the operation of fuel cells is confined to moderate temperatures. For example,

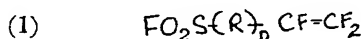
organic fuels such as methanol could not be used in a sulfuric acid/nitric acid system above about 40°C. because of membrane failure. At these temperatures, fuel cells using acid electrolytes did not have as high electrode potentials as fuel cells using alkaline electrolytes. Higher temperatures could not be used because the ion-exchange membranes failed and were decomposed by the acidic environment.

Furthermore, in electromechanical energy storage cells or secondary electromechanical cells, electrochemically regenerable oxidant solutions are employed as catholytes and electrochemically regenerable reductants are employed as anolytes with an ion-permeable membrane separating the catholyte from the anolyte. The hitherto known membranes used in such cells have all been characterized by deterioration of their physical and/or chemical properties during discharge of the cells to such an extent that they are not satisfactory for many practical applications.

By the term "electrochemical cells", as used in this specification, it is meant to include fuel cells as well as secondary electrochemical cells.

The ion-exchange membranes of this invention are stable to heat up to temperatures of 250°C. and to acidic conditions at such temperatures, thus allowing the use of higher temperatures in the operation of such electrochemical cells and increasing the lifetime of the cell. In addition, the membranes of this invention impart a greater operating efficiency to fuel cells utilizing acid electrolytes than do previously known membranes.

The novel ion-exchange membranes of this invention are thin films of fluorinated copolymers having pendant sulfonic acid groups. Specifically, the fluorinated copolymers are derived from monomers of the formula

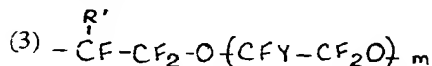


in which the pendant FO_2S — groups are converted to HO_3S — groups, and monomers of the formula



wherein:

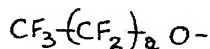
R represents the group



10 in which R' is fluorine or perfluoroalkyl of 1—10 carbon atoms, Y is fluorine or trifluoromethyl, and m is 1, 2 or 3,
 n is 0 or 1;

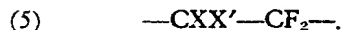
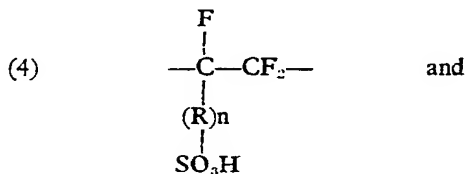
X is fluorine, chlorine, trifluoromethyl, or hydrogen; and

15 X' is X or



wherein a is 0 or an integer from 1 to 5.

20 Thus, the copolymers employed as membranes in the fuel cells of this invention contain recurring structural units of the formulas



25 The mole per cent of the sulfonic acid monomer of formula (1), and consequently of the resulting recurring structural unit of formula (4) will range between 3 and 20 mole per cent, and preferably between 6 and 15 mole per cent.

30 Copolymers of trifluorovinyl sulfonic acid, i.e., the monomer of formula (1) in which n is zero, are preferred because they will contain the greatest number of sulfonic acid groups per gram of polymer. Most preferred are copolymers of trifluorovinyl sulfonic acid and fluorinated ethylenes, especially tetra-
35 fluoroethylene.

The invention can be further understood by reference to the accompanying drawings, in which

40 Fig. 1 is a schematic drawing of a fuel cell containing electrolytes in the electrode chambers;

Fig. 2 is a schematic drawing of a fuel cell

containing dry electrode chambers in which the membrane acts as the acidic electrolyte;

Fig. 3 is a schematic drawing of a fuel cell containing an electrolyte in only one electrode chamber;

Fig. 4 is a schematic drawing of a secondary cell of the flow type; and

Fig. 5 is a front view of one of the electrolyte compartments of the cell of Fig. 4 showing the winding path of the electrolyte through the polytetrafluoroethylene separator sheet.

The novel membranes of this invention can be employed in the types of fuel cells represented by Figs. 1—3, in secondary cells represented by Figs. 4 and 5, and common variations of them.

The polymers used to prepare the membranes of this invention are obtained by polymerizing the monomers of formulas (3) and (4). In general, the monomers are polymerized in a perfluorocarbon solvent, such as perfluorodimethylbutane, although a solvent is not necessary if the monomers are liquid at the reaction temperature. A perfluorinated free radical initiator, such as N_2F_2 is used, and a temperature of 50° to 200°C . employed. Pressure is not critical, but generally super-atmospheric pressures are used to control the ratio of the comonomer $\text{CXX}'=\text{CF}_2$.

In preparing the copolymers of the fluorocarbon vinyl ethers, it is also possible to use aqueous media at a pH of 8 or lower and temperatures not above 110°C . The polymers are generally obtained in their sulfonic fluoride form and are converted to the sulfonic acid form by first reacting the resin with a strong base such as sodium hydroxide and then exchanging the resulting salt cation with hydrogen from a strong inorganic acid such as hydrochloric acid, nitric or sulfuric acid. These processes are more fully explained in British Specification No. 1,034,197 and in U.S. Patent No. 3,041,317.

The polymers are pressed into thin films ready for use as membranes in this invention before conversion of the pendant SO_2F groups to SO_3H groups. By simply pressing the polymer at 250—40,000 psig, coherent films of 1—15 mils thickness can be obtained. For use as electrochemical cell ion-exchange membranes, thicknesses of 1—10 mils are preferred. If desired, temperatures of 100° — 300°C . can be employed during the pressing step.

By the processes described above, a homogeneous resin membrane is obtained that is resistant to decomposition by strong acids and high temperatures. The homogeneous form of the film is preferred since thinner films can be obtained. However, the copolymer can be reinforced, if desired, by placing it on an inert binder known in the art.

The degree of sulfonation of the polymer is determined by equivalent weight tests; i.e.,

by titrating the resin in its acid form with standard 0.1N sodium hydroxide, the weight in grams of the polymer containing one gram equivalent of hydrogen ions (1.008 g.). The equivalent weights of the homogeneous resinous membranes of this invention vary from 1,000 to 4,000 depending upon the monomer, comonomer, and polymerization conditions. For most membranes herein, an equivalent weight range of 1,000 to 2,000 is preferred. Low equivalent-weight polymers are preferred for use as membranes because of better ion exchange and lower internal resistance and polarization in the electrochemical cell.

As a general rule, the ion-exchange resins which form the membranes of this invention are prepared or are converted to the acid form in aqueous solution. Thus, the membranes will be substantially saturated with water, making the H^+ ion extremely mobile. For this reason, the gaseous fuel cell depicted in Fig. 2 is considered to be a fuel cell which employs an acid electrolyte. The membrane acts in a dual capacity as the membrane and as the acid electrolyte.

The following examples illustrate the preparation of some of the membranes employed in this invention:

EXAMPLE A

Into a stainless steel shaker tube was charged 13 g. of trifluorovinyl sulfonyl fluoride, 30 ml of perfluorodimethylcyclobutane, and 10 g. of gaseous tetrafluoroethylene. A separate vessel of 60 ml volume was filled with a gaseous mixture of 2.2% by weight of N_2F_2 in nitrogen to a pressure of 630 mm Hg absolute. This mixture was then pushed into the reaction vessel by a stream of nitrogen gas. The reaction mixture was heated to 75°C. giving a total pressure of 900 psig. After 1.66 hours of agitation at this temperature, the pressure had dropped to 850 psig, and there was no further change in pressure during an additional 1.20 hours of heating.

The reaction mixture was cooled and transferred to a round bottom flask. Volatile components of the mixture were removed under vacuum while heating the flask with an infrared lamp. The residue of 13.5 g. of copolymer remained in the flask. The product was combined with 250 ml of water and cut in a high-speed blender. It was isolated by filtration, air dried, and passed through a 20 mesh screen.

In order to hydrolyze pendant $-SO_2F$ groups in the copolymer to $-SO_3Na$ groups, an 8.6 g portion of the copolymer was heated for 5 hours at 150°C. in the presence of a liquid medium consisting of 4 ml of 50% by weight aqueous sodium hydroxide solution, 80 ml of methanol and 10 ml of triethylamine. The hydrolyzed copolymer was recovered by filtration, washed with methanol and air dried.

The $-SO_3Na$ groups in the hydrolyzed

product were converted to $-SO_3H$ groups by an ion exchange reaction carried out as follows: The hydrolyzed copolymer was stirred in 150 ml of a 1:1 volumetric mixture of methanol and concentrated hydrochloric acid and heated under reflux for a period of 16 hours. The product was removed by filtration and washed with a 1:1 volumetric mixture of methanol and water. After vacuum drying at 85°C., 7.6 g. of copolymer containing $-SO_3H$ groups was recovered.

The presence of $-SO_3H$ groups was verified by titration as follows: A 0.9146 g. sample of the acid resin copolymer was mixed with 1 g. of sodium chloride and about 20 ml of a 1:1 volumetric mixture of methanol and water. The mixture was sparged with nitrogen, and 3 ml of standard 0.1 N sodium hydroxide was added. The mixture was stirred for several hours, and excess sodium hydroxide was determined by back titration with standard 0.1 N hydrochloric acid to the methyl red endpoint. The sample was found to contain 0.065 milli-equivalents of $-SO_3H$ groups, showing it to be an ion exchange resin having an equivalent weight of approximately 14,000.

To obtain a film, the copolymer is pressed at 275°C. before the hydrolysis step.

Employing the foregoing procedure, it is possible to prepare trifluorovinyl sulfonic acid resins containing higher or lower concentrations of polymerized trifluorovinyl sulfonic acid by employing higher or lower concentrations of trifluorovinyl sulfonyl fluoride in the polymerization. Vinyl fluoride, vinylidene fluoride, trifluoroethylene or chlorotrifluoroethylene can be substituted for the tetrafluoroethylene to obtain the corresponding copolymers.

EXAMPLE B

Into an evacuated stainless steel shaker tube was charged about 160 grams of perfluoro[2-(2-fluorosulfonylethoxy)-propyl vinyl ether] of the formula:



about 60 g. of tetrafluoroethylene, and about 100 g. of perfluorodimethylcyclobutane. A separate vessel of 60 ml volume was filled with a mixture of 2.2% by weight of N_2F_2 in nitrogen to a pressure of about 630 mm Hg absolute, and this mixture pushed into the reaction vessel with nitrogen gas. The mixture was shaken and the temperature raised slowly to 80° for a period of 1 hour. On cooling and discharging, 28 grams of 35 weight per cent vinyl ether copolymer having a melt viscosity above 1×10^4 poises was obtained.

This spongy mass was obtained by steam distillation of the residue to remove the unreacted vinyl ether monomer. The polymer was compression molded at a temperature of 200°C under pressures of about 40,000 lbs.

to form sheets of from 1 to 15 mils. in thickness. The polymer yielded a clear tough film which was thereafter treated in the solution described in Example A to form the salts of the sulfonic acid groups and thereafter hydrolyzed to yield an ion-exchange membrane having an equivalent weight of about 1,300.

5 Copolymers can be made, employing the monomer of the material described above with equivalent weights as low as 600.

10 Examples 1 through 4 demonstrate the use of the membranes in fuel cells of this invention.

15 In Examples 1—4, a fuel cell of the type depicted in Fig. 1 was employed. In this fuel cell, an anode (10) and a cathode (12) are immersed in electrolytes (14) and (16) respectively. The electrolytes are held in container 18 and are separated by ion-exchange membrane 20. Oxidant is supplied to the cathode 20 and fuel supplied to the anode 10. Electrical connection to the anode is made through lead 22 and to the cathode through lead 24, which leads are connected to a variable load or electrical resistance 26. A catalytic coating 28 can be placed on the electrodes.

25 In this type of cell, hydrogen gas or a fuel which is oxidized to yield hydrogen ions is absorbed in, or, in the case of the latter type of fuel, can itself be, the electrolyte. It oxidizes at the electrode catalyst surface giving up electrons to the inert anode. In the cathode compartment, oxygen in some form yields oxide anions which combine with hydrogen ions from the ion-exchange membrane. The electrolytes contact opposite sides of the membrane, thus maintaining it in a wetted condition.

40 In these examples, the cathode and anode employed were 20 cm². ferrosilicon disks prepared from a commercial ferrosilicon powder, containing 17% by weight silicon, which was

45 passed through a 140 mesh (U.S. Standard Sieve Series) screen, by sintering the powder in a graphite mold for 2 hours in a vacuum at 1050°C. The porous disk obtained was coated with platinum by placing the ferrosilicon disk in a dish containing aqueous Na₂PtCl₆ solution (0.059 gm. Pt/ml) and heating on a hot plate to about 85°C. and 50 maintaining the temperature until the reaction is completed i.e., until a clear solution is obtained. (These ferrosilicon electrodes are more fully described in U.S. Patent No. 3,297,487). Oxygen was supplied to the cathode in the 55 form of 70 weight per cent nitric acid as the electrolyte 16; while 12 volume per cent methanol in 30 weight per cent sulfuric acid was used as the fuel and electrolyte 14.

60 In these examples, the membrane employed was a copolymer prepared as in Example B using the monomers of Example B. The weight per cent of the —SO₃H containing monomer and of the copolymer units corresponding thereto was 29% (8.4 mol % sulphonic acid units). The polymer had an equivalent weight of about 1540.

EXAMPLE 1

70 The fuel cell was assembled as described above. It was found to have an open circuit voltage of 1.06 V. and at room temperature delivered 0.31 V. at 50 milliamperes/cm². over a period of 2 hours and 20 minutes. The temperature was raised to 90°C. and the cell 75 delivered 0.46 to 0.53 V. at 50 milliamperes/cm². over a total period of 8 hours and 10 minutes.

EXAMPLE 2

80 The cell used in Example 1 was employed again and found to have an open circuit voltage of 0.875 V. The temperature was raised in stages and at 50 milliamperes/cm². data was collected as follows:

85	Temperature (°C.)
	room
	48
	70
	80
	90

Operating voltage
0.25
0.295
0.38
0.44
0.53—0.49 over 7 hours
and 20 minutes

90 EXAMPLE 3

The fuel cell employed in Example 2 was used with fresh fuel and oxidant. Open circuit voltage was about 0.72 V. For 8 hours and 20 minutes, the cell ran at 90°C. delivering 95 0.56—0.485 V. at 50 milliamperes/cm².

EXAMPLE 4

100 With fresh fuel and oxidant, but the same electrodes and membrane, the cell of Example 3 delivered 0.535—0.49 V. at 50 milliamperes over a period of 6 hours and 50 minutes.

The operations of the foregoing examples were repeated with approximately the same voltage results until a total of about 100

105 hours of operation at 90°C. was attained with the membrane originally used in Example 1. After about 60 hours of operation, the cell was fitted with a gas lift pump and drain to provide a continuous flow of fuel and oxidant to the cell.

110 Gaseous fuel cells of the type depicted in Fig. 2 can also be employed. Ion-exchange membrane 40 can be positioned between and in electrical contact with anode 42 and cathode 44, and is the sole electrolyte in the cell. Leads 46 and 48 connect the anode 42 and 115 cathode 44, respectively, and deliver current to electrical resistance 50. Gaseous fuel, usually hydrogen, is supplied to anode 42

through inlet 52. The oxidant, usually air or oxygen, is supplied to the cathode 44 through inlet 54. The electrodes are plated with catalysts 56 and 58. In operation, the fuel and oxidant enter the respective chambers and penetrate the porous electrodes to contact the surface of the membrane. On the hydrogen side, electrons are given up and the hydrogen ions migrate to the cathode chamber where they combine with returning electrons in the presence of oxygen to form water. Thus, the water forms only in the cathode compartment, usually on the edges of the membrane, where it drops off and is carried out through outlet 60. If air is the oxidant, outlet 60 is also employed to remove the nitrogen which builds up. If a gaseous fuel such as alcohol, aldehydes or hydrocarbons, is used, the anode chamber can be provided with an outlet to remove the carbon dioxide which builds up.

A wet anode-dry cathode fuel cell as shown in Fig. 3 can also be employed with the membranes of this invention. This cell comprises an ion-exchange membrane 92 in contact with electrodes 70 and 72. Leads 74 and 76 in connection with these electrodes deliver power to standard resistance signified by 78. The electrodes are covered with catalysts designated as 80 and 82. Fuel gas or liquid is supplied to electrode 70 through inlet 84 in contact with acid electrolyte 86. An outlet 88 permits waste gases to exit from the electrolyte. The oxidant gas which may be oxygen or air is admitted into the cathode chamber via inlet 90 and in contact with cathode 72 reacts with protons coming through ion exchange membrane 92 at the catalytic surface of the cathode 72 to produce water and waste gases which are permitted to exit the cathode chamber via outlet 94.

The following examples illustrate the use of the membranes in secondary electrochemical cells of the invention.

In these examples, a secondary electrochemical cell of the type depicted in Figs. 4 and 5 was employed. In this cell a cation-permeable membrane 100 is held between two separator plates of polytetrafluoroethylene 102 which have electrolyte compartments cut out as illustrated in Fig. 5 to provide a path

for the flow of electrolyte through the cell. An anode 104 and a cathode 106 are placed next to the separator plates 102. When the cathode is a graphite plate, it is desirable to use a backing sheet of rubber to prevent cracking of the graphite plate when the cell elements are placed between non-conductive plastic plates 108 and the entire assembly is fastened together. The catholyte is introduced at 112 and the anolyte at 110, and after passing through the cell the spent solutions are withdrawn at 112' and 110', respectively. When the cell is being recharged, plate 104 becomes the cathode and plate 106 becomes the anode.

EXAMPLE 5

The secondary cell of the type shown in Figs. 4 and 5 was assembled with a plate (5 mils thick) of a copolymer of tetrafluoroethylene and perfluoro[2-(2-hydroxysulfonylethoxy)propyl vinyl ether], having a neutral equivalent of 1100 (i.e., the sulfonic acid-containing comonomer amounting to 13 mole per cent of the polymer) between the two polytetrafluoroethylene separator plates 102. In this particular cell, the separator plates are 7.5 cm. square and the electrolyte compartment is a path 3.2 mm. wide and 0.8 mm. deep cut into the plate, with total length of the path being 51 cm. The cross-section of the electrolyte solution, i.e., the area across which electric current is passed is 14.6 cm². An anode 104 of amalgamated zinc and a cathode 106 of graphite are placed next to the separator plates 102. A plate of rubber 114 is then placed on the outside of the graphite plate to prevent cracking the graphite when the cell elements are placed between plates 108 made of poly(methyl methacrylate). The entire assembly is then fastened tightly together by means of clamps. The anolyte is a 3M aqueous solution of sulfuric acid and the catholyte is 2M CrO₃ and 3M sulfuric acid in water. These electrolytes, at a temperature of 25°C., are passed through the cell at a rate of 1 cm³ per minute, and the spent solutions are withdrawn at outlets 110' and 112' respectively. The cell is discharged through a variable load (resistor) connected to the anode 3 and cathode 4. The cell voltage was measured as a function of cell current and the following results were obtained.

Cell Voltage	Current	Current Density	Power Density
volts	amp.	mA/cm ²	mW/cm ²
2.18	0	0	0
1.98	0.198	13.5	26.8
1.90	0.380	26.0	49.5
1.72	0.860	60.5	104
1.50	1.50	103	154
1.39	1.74	119	166
1.19	1.98	135	161
1.07	2.14	147	157
0.90	2.25	157	139

EXAMPLE 6

5 A secondary cell of the type described in Example 5 was used with the following specific components: anode, amalgamated zinc; anolyte, 5M aqueous LiBr solution; mem-

brane, same as in Example 5; catholyte, 2.5M Br₂ solution in 2M aqueous LiBr; cathode, graphite; temperature, 25°C.; flow rate of electrolytes, 1 cm³/minute. Discharge characteristics of this cell are shown below.

10

Cell voltage	Current	Current Density	Power Density
volts	amp.	mA/cm ²	mW/cm ²
1.96	0	0	0
1.92	0.019	1.3	2.5
1.76	0.176	12.0	21.2
1.60	0.320	21.9	35.0
1.43	0.476	32.6	46.6
1.24	0.620	42.5	52.6
1.11	0.740	50.7	56.3
0.93	0.930	63.7	59.4
0.82	1.020	70.0	57.2

EXAMPLE 7

15 The secondary cell described in Example 5 was assembled with the following specific components: anode, platinum; anolyte, 3M SnCl₂ in 6M aqueous HCl solution; mem-

brane, same as in Example 5; catholyte, 2M CrO₃ in 3M aqueous H₂SO₄ solution; cathode, graphite; temperature, 25°C.; flow rate of electrolytes, 1 cm³/minute. Discharge characteristics of the cell were as follows:

20

Cell Voltage	Current	Current Density	Power Density
volts	amp.	mA/cm ²	mW/cm ²
1.27	0	0	0
1.18	0.012	0.81	0.95
1.10	0.055	3.76	4.15
1.05	0.105	7.20	7.55
0.99	0.199	13.6	13.5
0.87	0.435	29.7	25.9
0.75	0.750	51.3	38.5
0.56	1.400	96.0	54.0

EXAMPLE 8

The secondary cell described in Example 5 was assembled with the following specific components: anode, mercury on copper base; anolyte, 1.7M CrCl₂ + 1.7M HCl + 0.85M

ZnCl₂ in aqueous solution, membrane, same as in Example 5; catholyte, 2M CrO₃ + 3M H₂SO₄ aqueous solution; cathode, graphite, temperature, 25°C. The discharge characteristics of this cell were:

Cell Voltage	Current	Current Density	Power Density
volts	amp.	mA/cm ²	mW/cm ²
Flow rate: 1 cm ³ /min.			
1.83	0	0	0
1.60	0.032	2.19	3.5
1.46	0.146	10.0	14.6
Flow rate: 2 cm ³ /min.			
1.34	0.268	18.3	24.6
Flow rate: 3 cm ³ /min.			
1.20	0.400	27.3	33.0

Thus, the ion-exchange membranes of this invention are useful in a wide variety of electrochemical cells employing many different oxidants and reductants.

A number of different types of electrodes are suitable for use in the anode and cathode compartments of the fuel cells of this invention. The electrode should be one which is a conductor, which will adsorb the fuel and will act as a catalyst for the electrode reaction. Suitable electrodes meeting these requirements are well known and many are described, for example, in "Catalysis, Inorganic and Organic", Berkman, Morrel, and Egloff, Reinhold Publishing Co., New York (1940). Suitable electrode materials include electrodes formed from metals of Group VIII

of the Periodic Table such as rhodium, palladium, iridium and platinum. Other suitable metals include nickel and copper. In addition to the electrodes formed of these metals, the electrodes can be formed of platinum or palladium block which is deposited on a base metal such as stainless steel, iron or nickel. In addition, suitable electrodes may be formed from metal oxides or from carbon which is activated with platinum or palladium, or with oxides of iron, magnesium, cobalt or copper. These electrode materials may be used in sheet form or in the form of screens, meshes, or porous metals. The electrodes may be solid supports coated with porous catalysts bound with organic materials and plastics. The thickness of the electrode is

not critical, sizes from 1 mil up to 1/4 inch or more have been operated satisfactorily as electrodes. In addition, the ferro-silicon electrodes described above can be employed.

5 The shape and configurations of the fuel cells of the invention are not limited to those indicated in Figs. 1—3. Effective design goals of portable fuel cells are realized by exposing the maximum of membrane and catalyst area to a minimum volume of electrolyte. Many shapes, arrangements and configurations for cell components have been devised to accomplish the said goals. One arrangement which can easily double and triple the area of exposed membranes is to corrugate or fold the electrode membrane laminate. Another method is to press the membrane in a relatively fluid state between two porous or spongy metal electrodes.

20 "Relatively fluid state" expresses a flow condition for the membrane so as to promote its penetration into the spongy metal electrodes. This condition can be obtained, for example, by swelling the membrane by soaking the sulonic acid form in sulfuric acid and carrying out the pressing operation on the swollen membrane.

Fuels commonly employed in fuel cells include hydrogen; alcohols, e.g., methanol; aldehydes such as formaldehyde; ketones such as acetone; organic acids, such as formic acid or acetic acid; hydrocarbons, such as methane and propane; or mixtures of the alcohols, aldehydes or ketones in mineral acids.

35 Oxidants commonly employed in fuel cells include oxygen, air, nitric acid, nitrogen dioxide and chlorine gas.

Similarly, a number of different types of electrodes are suitable as anodes and cathodes in the secondary cells of this invention. Suitable electrode materials, in addition to those illustrated in Examples 5—8, include all those mentioned previously for use in fuel cells of this invention. Specific examples of suitable electrode materials include Fe, Cd, Pd, Ni, Co, and Sn. As in the case of the fuel cells, the thickness of the electrodes of the secondary cells is not critical, thicknesses ranging from 1 mil up to 1/4 inch or more are satisfactory.

50 In addition to the specific electrolytes mentioned in Examples 5—8, the secondary cells of this invention can be operated with anolytes containing the following reducing

agents: U^{+3} , Eu^{+2} , V^{+2} , Ti^{+3} ; and catholytes containing the following oxidizing agents: Cu^{+2} , I_2 , Ce^{+4} , Co^{+3} , $S_2O_8^{+2}$, V^{+5} , and PbO_2 (reducible to Pb^{+2}). 55

The shape and configuration of the secondary cells are not limited to that illustrated in Figs. 4 and 5. Other commonly known shapes and sizes of secondary cells can be employed with ion-permeable membranes of the type defined hereinbefore used to separate the anolyte and catholyte compartments of the cells. Furthermore, any number of individual secondary cells of this invention can be combined in series or in parallel to provide the voltage and current desired for particular applications. 60

The great superiority of the copolymers of the type defined herein as ion-exchange membranes in the electrochemical cells of this invention is demonstrated by the following tests. Films of a copolymer of tetrafluoroethylene and perfluoro[2 - (2 - fluorosulfonylethoxy) propyl vinyl ether] (TFE/PSEPVE) of the type described in Example B and three of the best commercial membranes made by sulfonation of graft copolymers of styrene on polytetrafluoroethylene and polychlorotrifluoroethylene base films are used in these tests. The sulfonic acid content of the four membranes is determined by treating the membrane in acid form with a known amount of sodium hydroxide and treating the excess NaOH with standard hydrochloric acid using a glass electrode and/or methyl red as indicator. Samples of the four membranes are placed in a 2M CrO_3 , 3M sulfuric acid solution and refluxed at 100°C. for 24 hours. After washing out the excess acid and decomposition products from the treated films, the sulfonic acid contents of the membranes are again determined. The electrolytic conductivities of the four membranes, before and after treatment with the CrO_3 , sulfuric acid solutions, are also measured. From the results of these tests, which are summarized in the following table, it is evident that the membranes of the present invention exhibit no appreciable loss in sulfonic groups or change in electrolytic resistivity under these test conditions. On the other hand, the three commercial membranes lose substantial amounts of their sulfonic acid groups and the electrolytic resistivities of the membranes are increased markedly. 65 70 75 80 85 90 95 100 105

TABLE

Stability of Membranes in 2M CrO₃-3M Sulfuric Acids at 100°C. for 24 Hours

Membrane	Equivalent Weight Before Treatment Titration	Loss of Sulfonic Acid Groups	Resistance*: Ohm/cm ²	
			Before Treatment	After
TFE/PSEPVE (5 mils thick)	1200	None	1.7	1.7
Styrenesulfonic acid on poly- tetrafluoroethylene base (-1 mil thick)	570	99.5%	0.3	10,000
Styrenesulfonic acid on poly- chlorotrifluoroethylene base (10 mils thick)	1510	98%	2.2	465
Styrenesulfonic acid on poly- chlorotrifluoroethylene base (5 mils thick)	2240	58%	3.5	88

*Resistance measured at 1000 c.p.s. in 0.6M KCl solution.

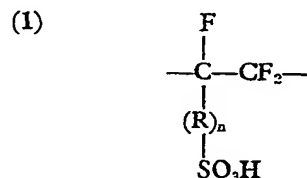
The copolymers of the type defined herein are stable under much more drastic conditions than those indicated in the above tests.

- 5 For example, a film of a copolymer of TFE and PSEPVE shows no detectable change in volume or electrolytic resistivity after immersion for three months at 100°C. in a 6N CrO₃-6N sulfuric acid solution. This film
- 10 is also essentially unchanged after immersion in 5N. potassium hydroxide for three months at 100°C.

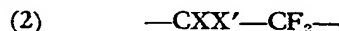
WHAT WE CLAIM IS:—

- 15 1. An electrochemical cell comprising a cathode and an anode and having a hydrated ion-exchange resin membrane separating the cathode from the anode, said resin being a film of fluorinated copolymer having pendant sulfonic acid groups.

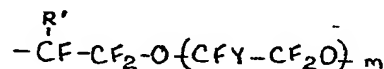
- 20 2. An electrochemical cell according to claim 1, in which the resin is a film containing a copolymer having recurring structural units of the formula:



and



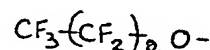
wherein R represents the group:



in which

R' is fluorine or perfluoroalkyl of 1 to 10 carbon atoms, Y is fluorine or trifluoromethyl, and m is 1, 2 or 3, n is 0 or 1; X is fluorine, chlorine, hydrogen or trifluoromethyl; and

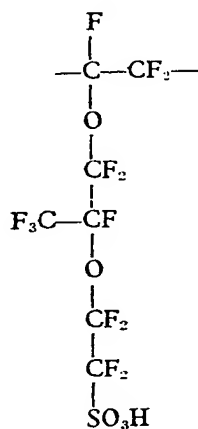
X' is X or



wherein a is 0 or an integer from 1 to 5; the units of formula (1) being present in an amount from 3 to 20 mole per cent.

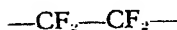
3. An electrochemical cell according to claim 2 wherein said copolymer has recurring structural units of the formula:

(1)



and

(2)



4. An electrochemical cell according to claim 2 or 3 wherein the units of formula (1) specified in claim 2 or 3 are present in an amount from 6 to 15 mole per cent.

5. An electrochemical cell according to claim 2 wherein said copolymer is a copolymer of tetrafluoroethylene and trifluorovinyl sulfonic acid.

6. An electrochemical cell according to any of claims 1 to 5 wherein the cathode comprises a catholyte and the anode comprises an anolyte.

7. An electrochemical cell according to any preceding claim which is a fuel cell for the generation of electrical current directly from a fuel and an oxidant.

8. An electrochemical cell according to any preceding claim substantially as herein described in the Examples.

9. An electrochemical cell according to any of claims 1 to 7 substantially as herein described with reference to and as illustrated in the accompanying drawings.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,

303/306, High Holborn, London, W.C.1.

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FIG. 1

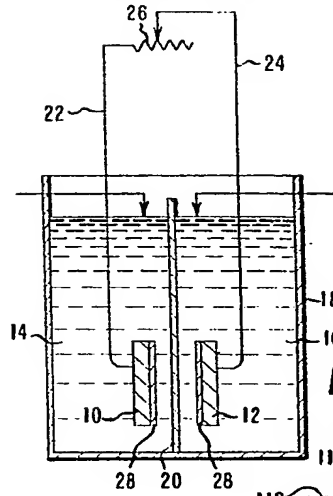


FIG. 2

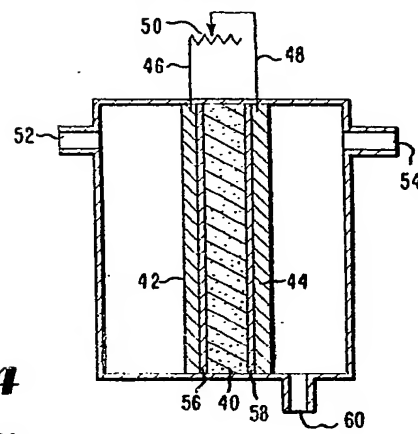


FIG. 4

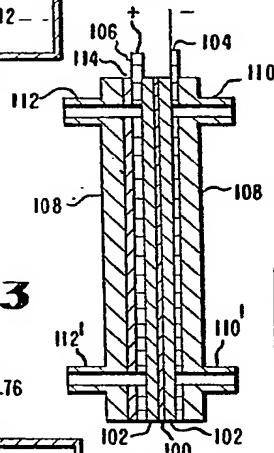


FIG. 3

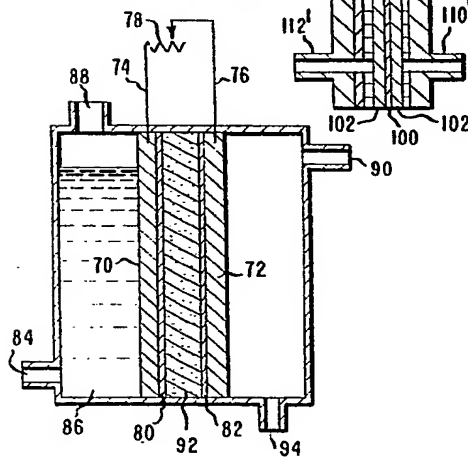
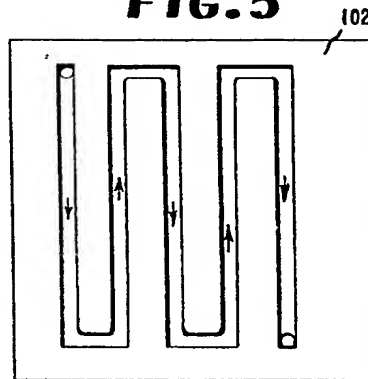


FIG. 5



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